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# TRANSLATION OF THE ANNEX TO THE IPER

25. The process of any one of claims 22 to 24, characterized in that reaction stages a<sub>1</sub>) and a<sub>2</sub>) are carried out at a temperature of from 40 to 120°C.

5 26. The process of claim 25, characterized in that the process is performed at a temperature of 50 to 110°C.

27. The process of any one of claims 22 to 26, characterized in that reaction stages a<sub>3</sub>) and b) are  
10 carried out at a temperature of from 10 to 60°C.

28. The process of claim 27, characterized in that the process is carried out at a temperature of 20 to 50°C.

15 29. The process of any one of claims 22 to 28, characterized in that reaction stages c<sub>1</sub>) and c<sub>2</sub>) are carried out at a temperature of from -20 to 50°C.

20 30. The process of claim 29, characterized in that the process is performed at a temperature of 0 to 30°C.

31. The use of the fluorine-modified polyurethane resins of claims 1 to 22 in the construction or industrial sector for the permanent oil- and water-  
25 repellent surface treatment or modification of mineral and nonmineral substrates.

32. The use of the fluorine-modified polyurethane resins of claim 31, characterized in that the mineral  
30 and nonmineral substrates are inorganic surfaces.

33. The use of the fluorine-modified polyurethane resins of claim 32, characterized in that the inorganic surfaces are, for example, porous, absorbent, rough and  
35 polished construction materials and building materials of all kinds (such as concrete, gypsum, silica and silicates, artificial stone, and natural stone (such as granite, marble, sandstone, slate, and serpentine),

clay, cement, brick) and also enamels, fillers and pigments, glass, ceramic, metals and metal alloys.

34. The use of the fluorine-modified polyurethane resins of claim 31, characterized in that the mineral and nonmineral substrates are organic surfaces.

35. The use of the fluorine-modified polyurethane resins of claim 32, characterized in that the organic surfaces are, for example, wood and woodbase materials, wood veneer, glass fiber-reinforced plastics (GRP), plastics, leather, natural fibers, polar organic polymers of all kinds, or composite materials.

36. The use of the fluorine-modified polyurethane resins of claims 1 to 22 for the permanent oil- and water-repellent surface treatment and/or modification in the construction sector.

37. The use of the fluorine-modified polyurethane resins of claim 36 as

- antigraffiti/antisoiling coatings
- easy to clean coatings
- coatings of all kinds
- seals
- prefabricated concrete components
- concrete moldings
- tiles and joints
- adhesives and sealants
- soundproofing walls
- corrosion control
- renders and decorative plasters
- external insulation and finishing systems (EIFS) and external insulation systems (EIS)

38. The use of the fluorine-modified polyurethane resins of claim 36 and 37, wherein coatings of all kinds comprise

- balcony coatings,
- roof(tile) coatings,
- baking varnishes,
- paints and varnishes,
- 5 • masonry paints,
- floor coatings,
- light-, medium- and heavy-duty industrial floors,
- carpark surfacings,
- sports floors.

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39. The use of the fluorine-modified polyurethane resins of claims 1 to 20 in the sector of

- automobile industry
- coil coatings
- 15 • baking varnishes
- glass facades and glass surfaces
- ceramics, including sanitary ceramics
- leather dressing
- surface-modified fillers and pigments
- 20 • paper coating
- rotors of wind turbines
- marine paints.

40. The use of the fluorine-modified polyurethane  
25 resins of claims 1 to 20 in the construction or industrial sector for the integral water/oil repellency treatment of concrete.

41. The concrete of claim 40, characterized in that it  
30 comprises concrete for prefabricated concrete components, concrete moldings, cast-in-place concrete, shotcrete, and ready-mix concrete.

### Claims

1. A fluorine-modified one- or two-component polyurethane resin, obtainable by

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a) preparing a fluorine-modified polyurethane prepolymer having free isocyanate groups or free amino and/or hydroxyl groups, or a fluorine-modified polyol mixture having free hydroxyl groups (binder), where

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a<sub>1</sub>) a fluorine-modified macromonomer (A1) having two or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 2000 daltons, a higher molecular mass polyol component (A2) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 500 to 6000 daltons, and, if desired, a low molecular mass polyol component (A3)(i) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons either

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is reacted with a polyisocyanate component (B)(i), consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity, in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst, or if desired, is blended in the presence of a solvent component (L)(i) and in the presence if desired of a catalyst,

a<sub>2</sub>) the fluorine-modified polyurethane prepolymer or polyol mixture from stage a<sub>1</sub>) is reacted if desired with an unmodified or fluorine-modified functionalizing component (C)(i) having one or more amino and/or hydroxyl groups that are reactive toward isocyanate groups and/or one or more isocyanate groups that are reactive toward hydroxyl groups and having a molecular mass of 50 to 2500 daltons, selected from the groups of the (cyclo)aliphatic and/or aromatic polyols and/or polyamines and/or polyamino alcohols and/or reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula  $(\text{RSiO}_{1.5})_n$  with  $n = 4, 6, 8, 10, 12$  and  $R =$  any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms and a molar mass of 250 to 25 000 daltons,

a<sub>3</sub>) the fluorine-modified polyurethane prepolymer or polyol mixture from stages a<sub>1</sub>) or a<sub>2</sub>) is admixed with a formulating component (F)(i),

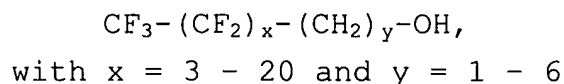
and finally

b) by preparing a fluorine-modified polyurethane resin having a polymer-bonded fluorine content of 1% to 4% by weight in the system as a whole by reacting the fluorine-modified polyurethane prepolymer from stage a<sub>3</sub>) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane prepolymer or polyol mixture from stage a<sub>3</sub>) (binder) in the case of a two-component application with a crosslinker component (D) (curing agent), with a formulating component (F)(ii) in the presence if desired of a solvent component (L)(iii) and also of a catalyst, using

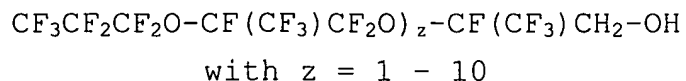
as crosslinker component (D) in the case of the polyol mixture from stage a<sub>3</sub>) a polyisocyanate component (B)(iii) consisting of at least one diisocyanate, polyisocyanate, polyisocyanate derivative or polyisocyanate homolog having two or more (cyclo)aliphatic or aromatic isocyanate groups of same or different reactivity and in the case of the polyurethane prepolymer a polyisocyanate component (B)(iii) or a low molecular mass polyol component (A3)(ii) having two or more hydroxyl groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 499 daltons and/or a low molecular mass polyamine component (E) having two or more (cyclo)aliphatic or aromatic amino groups that are reactive toward isocyanate groups and having a molecular mass of 50 to 500 daltons.

2. The fluorine-modified polyurethane resin of claim 1, characterized in that the fluorine-modified monomer (A1) has been prepared by

c<sub>1</sub>) reacting a fluoro alcohol component (A4) consisting of a perfluoroalkyl alcohol having terminal methylene groups (hydrocarbon spacers), of the general formula

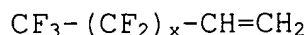


or of a hexafluoropropene oxide (HFPO) oligomer alcohol of the general formula



or else mixtures of these having a hydroxyl group that is reactive toward isocyanate groups and

- having a molecular mass of 250 to 5000 daltons,  
with a polyisocyanate component (B)(ii) consisting  
of at least one diisocyanate, polyisocyanate,  
polyisocyanate derivative or polyisocyanate  
5 homolog having two or more (cyclo)aliphatic or  
aromatic isocyanate groups of same or different  
reactivity, in the presence if desired of a  
solvent component (L)(ii) and in the presence if  
desired of a catalyst,
- 10 c<sub>2</sub>) if desired, reacting the preadduct from stage c<sub>1</sub>)  
completely with a functionalizing component  
(C)(ii) having two or more amino and/or hydroxyl  
groups that are reactive toward isocyanate groups  
15 and having a molecular mass of 50 to 500 daltons,  
selected from the group of (cyclo)aliphatic and/or  
aromatic polyols and/or polyamines and/or  
polyamino alcohols.
- 20 3. The fluorine-modified polyurethane resin of claim  
1 or 2, characterized in that as fluorine-modified  
macromonomer (A1) use is made of reaction products  
and/or macromonomers, with a monomodal molar mass  
distribution, of monofunctional perfluoroalkyl  
25 alcohols, isophorone diisocyanate or toluene  
diisocyanate, and diethanolamine.
4. The fluorine-modified polyurethane resin of claim  
1, characterized in that as fluorine-modified  
30 macromonomer (A1) use is made of optionally solvent-  
containing reaction products of
- i) perfluoroalkylalkenes and diethanolamine,  
preferably perfluoroalkylalkenes having terminal  
35 methylene groups (hydrocarbon spacers), of the  
general formula





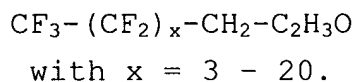
with x = 3 - 20

and/or

5    ii)    alkyl            (per) fluoro(meth)acrylates            and/or  
              (per) fluoroalkyl            (meth)acrylates            and/or  
              (per) fluoroalkyl    (per) fluoro(meth)acrylates    and  
              diethanolamine

10            and/or

              iii) (per) fluoroalkylalkylene oxides    and    N-methyl-  
                      ethanolamine    or    diethanolamine    with preferred  
                      (per) fluoroalkylalkylene oxides    of the general  
15            formula



20    5.    The fluorine-modified polyurethane resin of any  
          one of claims 1 to 4, characterized in that use is made  
          as higher molecular mass polyol component (A2) of  
          (hydrophobically modified) polyalkylene glycols,  
          aliphatic or aromatic polyesters, polycaprolactones,  
25    polycarbonates, hydroxy-functional macromonomers and  
          telecheles such as  $\alpha,\omega$ -polymethacrylatediols,  $\alpha,\omega$ -  
          dihydroxyalkylpolydimethylsiloxanes, hydroxy-functional  
          epoxy resins, hydroxy-functional ketone resins,  
          hydroxy-functional polysulfides, hydroxy-functional  
30    triglycerides, oxidatively drying alkyd resins based on  
          bisepoxides and unsaturated fatty acids, or mixtures  
          thereof.

          6.    The fluorine-modified polyurethane resin of any  
35    one of claims 1 to 4, characterized in that use is made  
          as component (A2) of linear and/or difunctional  
          (hydrophobically modified) polyether- and/or polyester-  
          and/or polycaprolactone- and/or polycarbonate-polyols

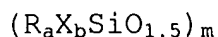
and/or  $\alpha,\omega$ -polymethacrylatediols having a molecular mass of 500 to 3000 daltons.

7. The fluorine-modified polyurethane resin of any one of claims 1 to 6, characterized in that use is made as component (A3)(i) and (A3)(ii) of 1,4-butanediol and/or 2-methyl-1,3-propanediol and/or 2,2-dimethyl-1,3-propanediol.

8. The fluorine-modified polyurethane resin of any one of claims 1 to 7, characterized in that use is made as components (B)(i) and/or (B)(ii) and/or (B)(iii) of difunctional polyisocyanate derivatives and/or reaction products of at least trifunctional aliphatic or aromatic polyisocyanates and optionally fluorine-modified amino-functional polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula  $(\text{RSiO}_{1.5})_n$  with  $n = 4, 6, 8, 10, 12$  and  $R =$  any organic residue having 1 to 100 C atoms and 0 to 50 N and/or 0 to 50 O and/or 0 to 50 F and/or 0 to 50 Si and/or 0 to 50 S atoms.

9. The fluorine-modified polyurethane resin of any one of claims 1 to 8, characterized in that component (C)(i) comprises reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula  $(\text{RSiO}_{1.5})_8$  with  $R =$  aminopropyl and/or isocyanatopropyl and optionally  $\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$  and/or H and/or  $\text{C}_1\text{-C}_{25}$ -alkyl and/or  $\text{C}_3\text{-C}_{25}$ -cycloalkyl and/or  $\text{C}_6\text{-C}_{30}$ -aryl and/or  $(\text{CH}_2)_3(\text{OCH}_2\text{CH}_2)_n\text{OMe}$  and/or epoxypropyl and/or dimethoxysilyloxy and/or methacryloyloxypropyl and/or triethoxysilylpropyl.

10. The fluorine-modified polyurethane resin of any one of claims 1 to 9, characterized in that use is made as component (C)(i) of reactive polyhedral oligomeric polysilsesquioxanes (POSS) of the general formula



with a = 0 or 1

b = 0 or 1

5 a+b = 1

m = 4, 6, 8, 10, 12,

and

10 R = hydrogen atom, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl or cycloalkynyl group or polymer unit, which in each case is substituted or unsubstituted, or further functionalized polyhedral oligomeric silicon-oxygen cluster units, which are attached via a polymer unit or a bridging unit,

15 X = oxy, hydroxy, alkoxy, carboxy, silyl, alkylsilyl, alkoxysilyl, siloxy, alkylsiloxy, alkoxysiloxy, silylalkyl, alkoxysilylalkyl, alkylsilylalkyl, 20 halogen, epoxy, ester, fluoroalkyl, isocyanate, blocked isocyanate, acrylate, methacrylate, nitrile, amino, phosphine or polyether group or substituents of type R that contain at 25 least one such group of type X,

the substituents of type R and the substituents of type X each being identical or different.

30 11. The fluorine-modified polyurethane resin of any one of claims 1 to 10, characterized in that (cyclo)aliphatic and/or aromatic polyamines and/or amino alcohols are used as low molecular mass polyamine component (E).

35 12. The fluorine-modified polyurethane resin of any one of claims 1 to 11, characterized in that latent curing agents based on aldimines and/or ketimines

and/or enamines are used as low molecular mass polyamine component (E).

13. The fluorine-modified polyurethane resin of any one of claims 1 to 12, characterized in that as formulating component (F)(i) and (F)(ii) use is made of defoamers, devolatilizers, lubricity and flow-control additives, dispersing additives, substrate wetting additives, water repellents, rheology additives, coalescence assistants, matting agents, adhesion promoters, antifreeze agents, antioxidants, UV stabilizers, bactericides, fungicides, further polymers, and also fillers, pigments, nanoparticles or a suitable combination thereof.

14. The fluorine-modified polyurethane resin of any one of claims 1 to 13, characterized in that the NCO/OH equivalent ratio of components (A1), (A2), (A3)(i), and (B)(i) in stage a) is set at a level of 0.5 to 10.0, preferably 1.5 to 6.0.

15. The fluorine-modified polyurethane resin of any one of claims 1 to 14, characterized in that the NCO/OH equivalent ratio of components (A4) and (B)(ii) in stage c<sub>1</sub>) is set at 1.9 to 2.1 and the NCO/OH+NH equivalent ratio of the components in the preadduct from stage c<sub>1</sub>) and (C)(ii) in stage c<sub>2</sub>) is set at 0.95 to 1.05.

16. The fluorine-modified polyurethane resin of any one of claims 1 to 15, characterized in that the NCO/OH equivalent ratio of binder and curing agent in stage b) is set at a level of 1.0 to 2.0, preferably 1.0 to 1.5.

17. The fluorine-modified polyurethane resin of any one of claims 1 to 16, characterized in that reaction stages a), b), and c) are carried out in the presence of 0.01% to 1% by weight, based on components (A) and

(B), of a catalyst which is customary for polyaddition reactions with polyisocyanates.

18. The fluorine-modified polyurethane resin of any  
5 one of claims 1 to 17, characterized in that in stage  
a) the solids content of fluorine-modified polyurethane  
prepolymer or polyol mixture, consisting of components  
(A1), (A2), (A3)(i), (B)(i), and (C)(i), is set at 25%  
to 100% by weight based on the total amount of the  
10 binder, consisting of components (A1), (A2), (A3)(i),  
(B)(i), optionally (C)(i), (F)(i), optionally (L)(i)  
and optionally (L)(iii).

19. The fluorine-modified polyurethane resin of claim  
15 18, characterized in that in stage a) the solids  
content of fluorine-modified polymethane prepolymer or  
polyol mixture is set at 50% to 75% by weight, based on  
the total amount of the binder.

20. The fluorine-modified polyurethane resin of any  
one of claims 1 to 19, characterized in that in stage  
b) the solids content of crosslinker component,  
consisting of components (B)(iii) and (B)(iii) or  
(A3)(ii) and/or (E), respectively, is set at 25% to  
25 100% by weight, based on the total amount of curing  
agent (D), consisting of components (B)(iii) or  
(A3)(ii) and/or (E), (F)(ii) and, if desired, (L)(iii).

21. The fluorine-modified polyurethane resin of claim  
30 20, characterized in that in stage b) the solids  
content of crosslinker component is set at 50% to 75%  
by weight, based on the total amount of the curing  
agent (D).

22. The fluorine-modified polyurethane resin of any  
35 one of claims 1 to 21, characterized in that the  
polyurethane polymer, consisting of components (A),

(B), (C), and (E), has an average molecular mass (number average) of 10 000 to 100 000 daltons.

23. A process for preparing the fluorine-modified polyurethane resin of claims 1 to 22, characterized in that

a) a fluorine-modified polyurethane prepolymer or polyol mixture (binder) is prepared by

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a<sub>1</sub>) reacting components (A1), (A2), and (A3)(i) either with component (B)(i) in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst, some or all of the hydroxyl groups of components (A1), (A2), and (A3)(i) being reacted with the isocyanate groups of component (B)(i), or blending said components in the presence if desired of a solvent component (L)(i) and in the presence if desired of a catalyst,

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a<sub>2</sub>) if desired, reacting the fluorine-modified polyurethane prepolymer or the polyol mixture from stage a<sub>1</sub>) with an optionally fluorine-modified functionalizing component (C)(i),

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a<sub>3</sub>) admixing the fluorine-modified polyurethane prepolymer or polyol mixture from stages a<sub>1</sub>) or a<sub>2</sub>) with a formulating component (F)(i), the formulating constituents being added individually or together before, during or after the reaction or blending of the individual components, and

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b) a fluorine-modified polyurethane resin is prepared by reacting the fluorine-modified polyurethane prepolymer from stage a<sub>3</sub>) in the case of a one-component application with atmospheric moisture, or reacting the fluorine-modified polyurethane

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prepolymer or polyol mixture from stage a<sub>3</sub>)  
(binder) in the case of a two-component  
application with a crosslinker component (D)  
(curing agent), a formulating component (F)(ii),  
5 and, if desired, a solvent component (L)(iii), in  
the presence if desired of a catalyst, using as  
crosslinker component (D) in the case of the  
polyol mixture a polyisocyanate component (B)(iii)  
and in the case of the polyurethane prepolymer a  
10 polyisocyanate component (B)(iii) or a low  
molecular mass polyol component (A3)(ii) and/or a  
low molecular mass polyamine component (E), and  
adding the formulating constituents individually  
or together before, during or after the blending  
15 of the individual components.

24. The process of claim 23, characterized in that the  
fluorine-modified macromonomer (A1) is prepared by

- 20 c<sub>1</sub>) reacting a fluoro alcohol component (A4) with the  
polyisocyanate component (B)(ii) in the presence  
if desired of a solvent component (L)(ii) and in  
the presence if desired of a catalyst, the  
reaction conditions and the selectivities of  
25 components (A4) and (B)(ii) being chosen such that  
only one isocyanate group of component (B)(ii)  
reacts with component (A4), and subsequently
- c<sub>2</sub>) if desired, reacting the preadduct from stage c<sub>1</sub>)  
30 completely with the functionalizing component  
(C)(ii), the reaction conditions and the  
selectivity of component (C)(ii) being chosen such  
that only one reactive group of component (C)(ii)  
reacts with the free isocyanate group(s) of the  
35 preadduct.